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VOLUME 32 JULY 1954 NUMBER 4

THE INTEGRAL HEATS OF VAPORIZATION OF ALCOHOL–WATER MIXTURES[1]

BY A. C. PLEWES, D. A. JARDINE, AND R. M. BUTLER

ABSTRACT

Integral heats of vaporization at constant composition were measured for methanol, ethanol, and *n*-propanol–water mixtures at pressures of 760 and 300 mm. Enthalpy–concentration charts were prepared from these data for distillation studies. Liquid–vapor measurements for the three systems indicated considerable deviation from Raoult's law, yet integral heats of solution obtained from the enthalpy correlations were small. A qualitative explanation for the behavior of the liquid mixtures is offered.

INTRODUCTION

Enthalpy–concentration data for mixtures are valuable in the solution of problems concerning evaporation, heat exchange, and distillation. Pioneer studies in these fields of endeavor were made by Ponchon (15) and Savarit (17) and their methods have been accepted in fields involving liquid–vapor exchange.

During a recent investigation it became necessary to obtain integral heats of vaporization of some alcohol–water mixtures. A literature search indicated that such data were lacking and it became necessary to determine the required information.

For purposes of record it was found that Bosnjakovic (1) prepared enthalpy–concentration charts for ethanol–water, ammonia–water, and calcium chloride–water in the liquid and vapor phases. Sulphur trioxide – water enthalpy data have also been published by Ross (16). Dana made accurate measurements of the heats of vaporization of liquid oxygen–nitrogen mixtures and this classic work has been used extensively in the production of industrial oxygen (3).

The present work concerned the measurement of the integral heats of vaporization of methanol, ethanol, and *n*-propanol–water mixtures and the preparation of enthalpy–concentration diagrams from the experimental results.

[1]*Manuscript received February 2, 1954.*
Contribution from the Department of Chemical Engineering, Queen's University, Kingston, Ontario.

EXPERIMENTAL EQUIPMENT AND PROCEDURE

The apparatus shown in Fig. 1 is a modification of a unit conceived and described by Dana (3). Simply stated the calorimeter vaporizes liquid feed at constant composition with a known wattage; that is, all feed entering the apparatus is vaporized thus assuring no change in composition at a given pressure.

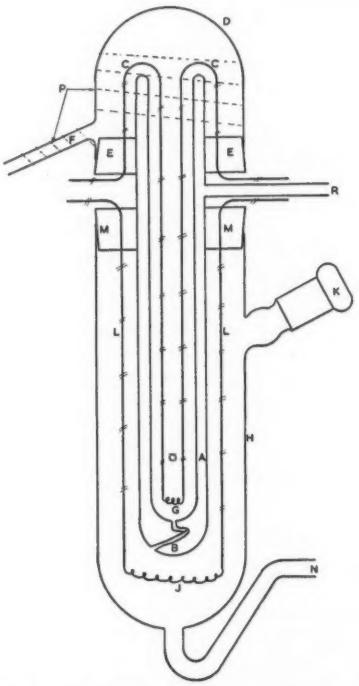

FIG. 1. Heat of vaporization apparatus.

A study of the calorimeter indicates three concentric chambers, *O*, *A*, and *H*, arranged in the unit. *O* is the calorimeter proper in which liquid feed is boiled by a given amount of electrical energy supplied by heater *G*. The leads *CC* are made of heavy copper wire to minimize potential drop to the heater. Vapors generated in *O* are led to a condenser and collecting vessel through side arm *F*.

Vessel *A* is a silvered glass tube which is evacuated during a run. This ensures an adiabatic condition for *O* and so prevents heat transfer in or out of the calorimeter. Vessel *H* acts as a preheater for the liquid feed and supplies material at a constant rate to *O* through capillary *B*. During operation the liquid enters *N* from a constant head device and mixes with the boiling fluid. Heater *J* supplies electrical energy for *H* and the vapors produced are liquified in a condenser attached at joint *K*.

A glass cap *D* heated externally with nichrome element *P* covers the top

of units *A* and *O*. Rubber stoppers *E* and *M* close vessels *H* and *D* from the atmospheric surroundings. Pressure in *H* and *O* was maintained carefully at 760 or 300 mm.

Power from a 12 volt storage cell was delivered to the nichrome heating element *G* and controlled by a suitable rheostat. The wattage was measured by a calibrated voltmeter and ammeter and the maximum error in energy evaluation amounted to ± 1.5%. Fluctuations in power were minimized by delivery of the direct current from laboratory mains to the battery so that the current entering the cell was approximately the same as that used in heater *G*.

The apparatus shown in Fig. 1 is 6 in. high and 2 in. wide. Best results were obtained if not more than 3 cc. of distillate were produced per minute. Beyond that point entrainment occurred and obscured the accuracy of measurement.

The model described was tested with pure starting materials and satisfactory results were obtained as shown in Table I. In the case of mixtures it

TABLE I

HEATS OF VAPORIZATION OF PURIFIED MATERIALS AT 760 MM.

Compound	Author's data, joules/gm.	Literature, joules/gm.
Methanol	1105	1100 (7)
Ethanol	858	855 (7)
n-Propanol	697	688 (7)
Water	2240	2258 (9)

became evident that steady state conditions were established in two to four hours, and that the time was dependent on the mixture used. The steady state condition was determined by analyses of the feed and distillate; in this state these two compositions agreed within 0.1%.

Analyses of the liquid mixtures were made by accurate density measurements, and the composition was obtained from data listed in the literature (6, 2).

Methanol was received as Analar reagent from British Drug Houses and was purified by the method of Morton and Mark (14). The middle two-thirds of the distillate from this treatment was redistilled over quicklime in a 5 ft. Podbielniak column using high reflux ratios.

Ethanol was prepared from the anhydrous material received from the Canadian Industrial Alcohol Company. This was purified by the method of Stout and Schuette (18). It was then redistilled in a 2 in. glass column packed for 6 ft. with 1/4 in. pyrex glass helices and dried over quicklime. A final distillation gave a satisfactory product.

n-Propanol obtained from British Drug Houses was freed of allyl alcohol by the procedure of Kretschmer (12). Distillation from anhydrous potassium carbonate gave a pure product. All alcohols were stored in brown glass bottles and in the presence of cylinder nitrogen.

City water was once distilled and used without further treatment.

EXPERIMENTAL RESULTS

The results of this study are shown in Table II for mixtures of water and methanol, ethanol, and *n*-propanol at pressures of 760 and 300 mm. The data obtained for ethanol were compared with values determined by Bosnjakovic (1) and good agreement was found to exist. No data for aqueous mixtures of methanol and *n*-propanol could be found in the literature and it is believed that the present results represent the first published information of this kind.

TABLE II

INTEGRAL HEATS OF VAPORIZATION OF ALCOHOL–WATER MIXTURES, JOULES PER GRAM

Methanol		Ethanol		*n*-Propanol	
Wt. % methanol in feed	$\lambda_{obs.}$	Wt. % ethanol in feed	$\lambda_{obs.}$	Wt. % *n*-propanol in feed	$\lambda_{obs.}$
Data from runs at 760 mm.					
10.9	2150	9.8	2170	9.2	2160
21.1	2050	18.5	2100	13.1	2140
30.1	2000	29.5	1920	22.2	2020
31.7	1970	42.2	1710	32.5	1810
38.9	1890	58.8	1460	43.2	1610
53.2	1740	67.7	1320	52.2	1470
62.6	1620	78.7	1150	57.9	1360
70.5	1500	89.6	980	66.6	1210
89.8	1240	92.2	990	74.7	1080
Data from runs at 300 mm.					
9.3	2240	10.0	2260	9.8	2180
20.8	2110	21.3	2120	23.0	1960
30.7	2020	30.2	1940	32.5	1820
39.8	1890	40.1	1750	42.2	1660
50.1	1780	50.6	1630	53.2	1460
58.8	1690	64.8	1400	61.0	1350
68.6	1570	74.4	1240	70.9	1160
78.0	1430	82.2	1130	79.4	1030
86.5	1320	86.5	1070	88.8	900

From heats of vaporization data it was possible to construct enthalpy–concentration diagrams as shown in Figs. 2–7. These charts are most useful for the correlation of the physical properties of liquid and vapor mixtures, and are prepared often for exact distillation calculations.

The construction of the diagram is reviewed briefly and presupposes the following facts:

(1) The enthalpy of each pure component in the liquid state is zero at 0°F.

(2) The specific heats (7, 8, 10, 11) and latent heats of the pure components are available.

(3) The integral latent heats of the mixtures are known.

(4) The heats of solution of the gaseous mixtures are small or approach zero.

(5) Boiling point – composition data are available for the mixtures at a given pressure (13).

Starting at 0°F. for each component it is possible to estimate the enthalpy of the pure liquids up to the boiling point at a given pressure. The addition of the latent heats of either component at a given temperature to the liquid enthalpy yields a point in the vapor state. If it is assumed that the vapors mix without heat change, the isotherms connecting the enthalpies of the pure components can be drawn as straight lines. This has been done for several temperatures in the vapor region as is shown in Figs. 2–7.

From boiling point – composition data (13) it is possible to select a point on the dew line and subtract the integral latent heat of vaporization for the mixture. The resultant enthalpy gives a point on the boiling or liquid curve. This was done over the complete range of composition for the three mixtures at 760 and 300 mm. Tie lines and conjugates are indicated also on this diagram showing the temperature of the boiling solution and the composition of vapor in equilibrium with the liquid.

The heat of mixing of any mixture at its boiling point was determined by drawing in an ideal isotherm at the same temperature as the mixture. The enthalpy difference between the two plots at a given composition gave the integral heat of solution at a stated pressure. The data obtained for ethanol were compared with those of Bosnjakovic (1) and Dodge (4) and good agreement was found. However, the values shown in Tables III–V are small and the error in the measurements of the heats of vaporization makes these results of qualitative significance only. The fact that our results did check those of other authorities speaks well for our heats of vaporization.

From the data found at the boiling points of the solutions other heats of solution were estimated at lower temperatures from specific heat data. These facts were used to estimate points on various isothermal liquid lines.

TABLE III

METHANOL–WATER

HEATS OF SOLUTION–q_s–JOULES/MOLE

Mole % methanol	760 mm. q_s Author	300 mm. q_s Author
0	0	0
10	−350	−300
20	4310	150
30	890	620
40	1000	900
50	980	1090
60	800	1180
70	560	1100
80	350	920
90	200	600
100	0	0

TABLE IV

ETHANOL–WATER
HEATS OF SOLUTION–q_s–JOULES/MOLE

Mole % ethanol	760 mm.		300 mm.	
	q_s Author	q_s Bosnjakovic	q_s Dodge	q_s Author
0	0	0	0	0
10	520	350	83	570
20	170	−100	−39	600
30	−170	−250	−209	400
40	−350	−350	−342	70
50	−450	−450	−390	−100
60	−450	−490	−390	−100
70	−380	−490	−345	−100
80	−280	−450	−235	−70
90	−120	−300	−145	−30

TABLE V

PROPANOL–WATER
HEATS OF SOLUTION–q_s–JOULES/MOLE

Mole % propanol	760 mm. q_s	300 mm. q_s
0	0	0
10	850	300
20	300	−120
30	−120	−310
40	−510	−500
50	−880	−670
60	−1110	−750
70	−1310	−750
80	−1340	−680
90	−1130	−450

It is interesting to study the heats of solution calculated from these charts. A summary of results is shown in Tables III–V for the three alcohol–water mixtures at pressures 760 and 300 mm. The heat effect shown follows the convention employed by Dodge (4), and means that a positive sign indicates heat evolution. It will be observed in all cases that heating and cooling effects were obtained for each mixture but these were small. The fact that exothermic and endothermic effects were observed in certain concentrations indicates that a combination of associating and dissociating reactions may be occurring in these solutions and that one reaction is slightly favored in one region relative to the other.

It is realized that mixtures that indicate small heat changes on mixing may not be ideal. Thus Guggenheim (5) states that zero heat of mixing is not a sufficient condition for ideality, but shows from statistical mechanics that similar size of molecules is another most important criterion for ideal solutions.

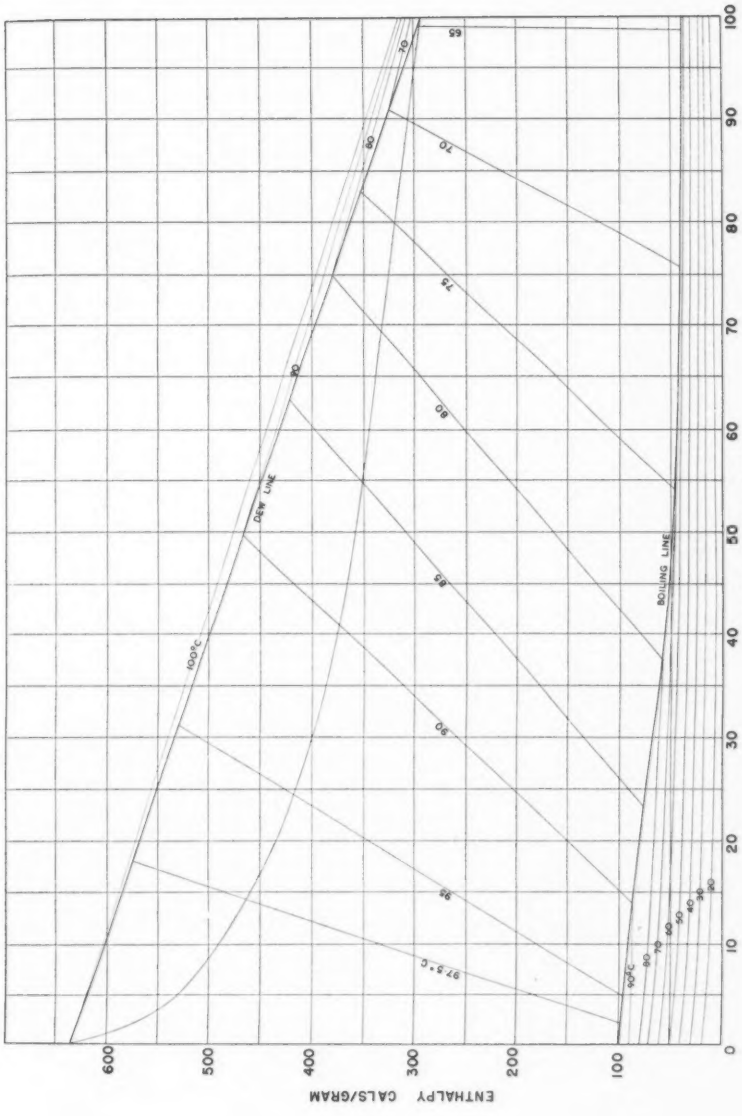

FIG. 2. Enthalpy-concentration diagram for methanol-water mixtures at 760 mm.

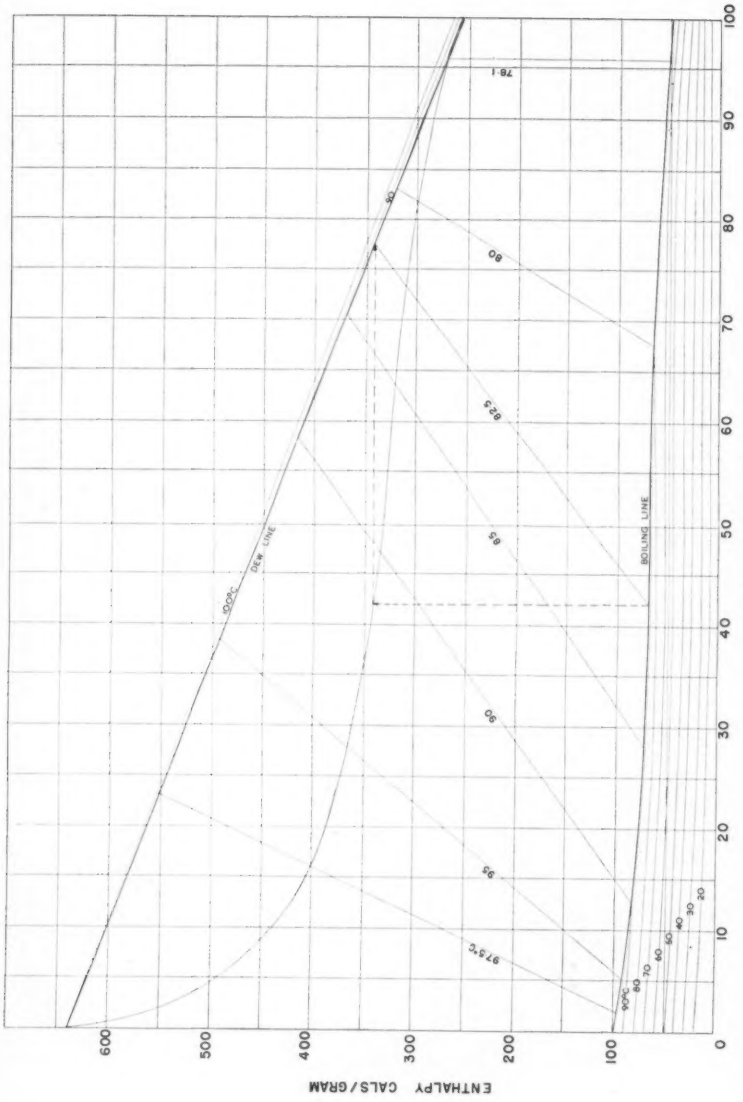

FIG. 3. Enthalpy–concentration diagram for ethanol-water mixtures at 760 mm.

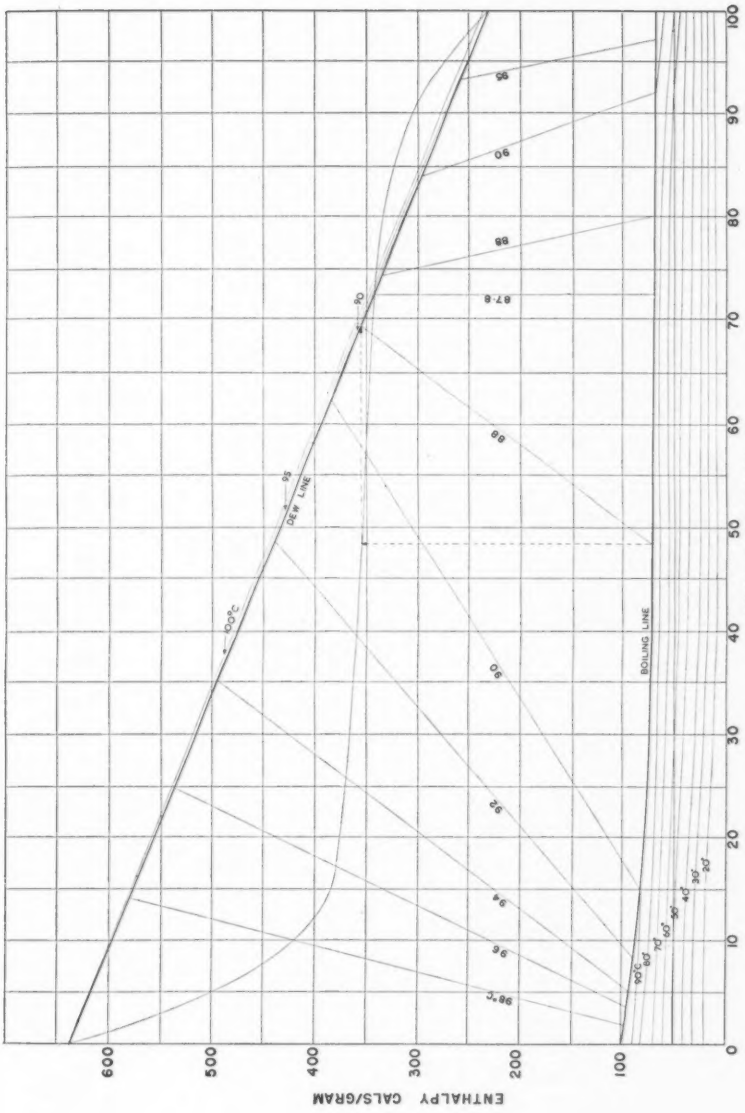

FIG. 4. Enthalpy–concentration diagram for *n*-propanol–water mixtures at 760 mm.

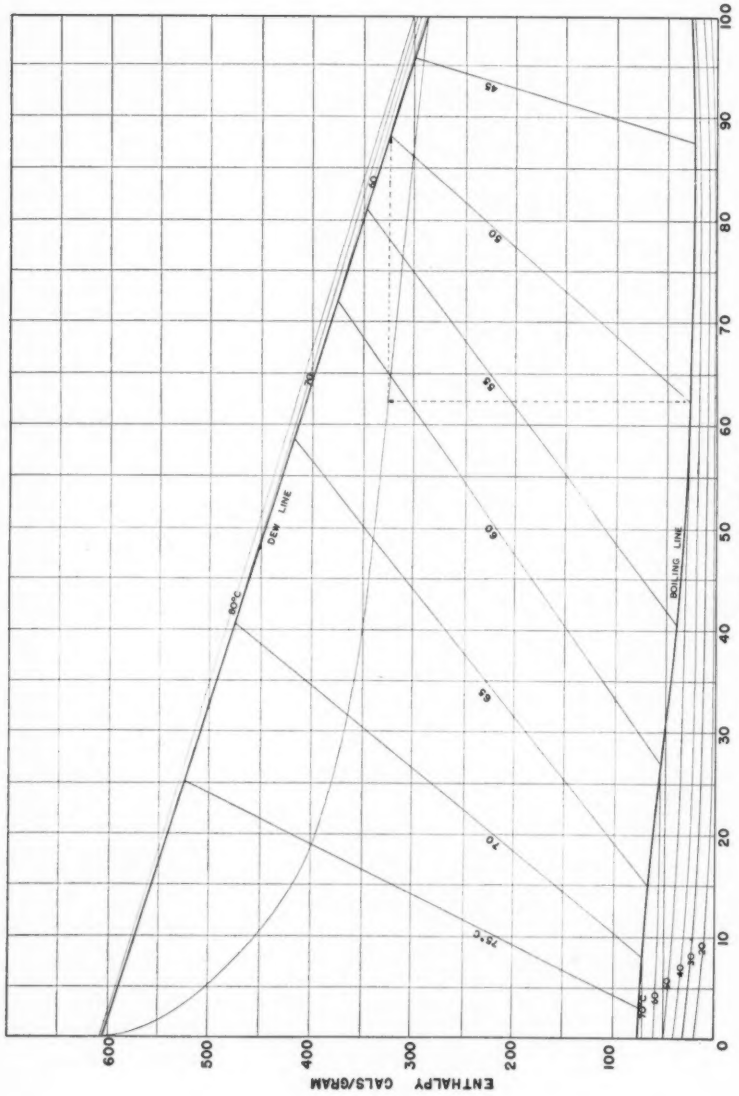

FIG. 5. Enthalpy–concentration diagram for methanol–water mixtures at 300 mm.

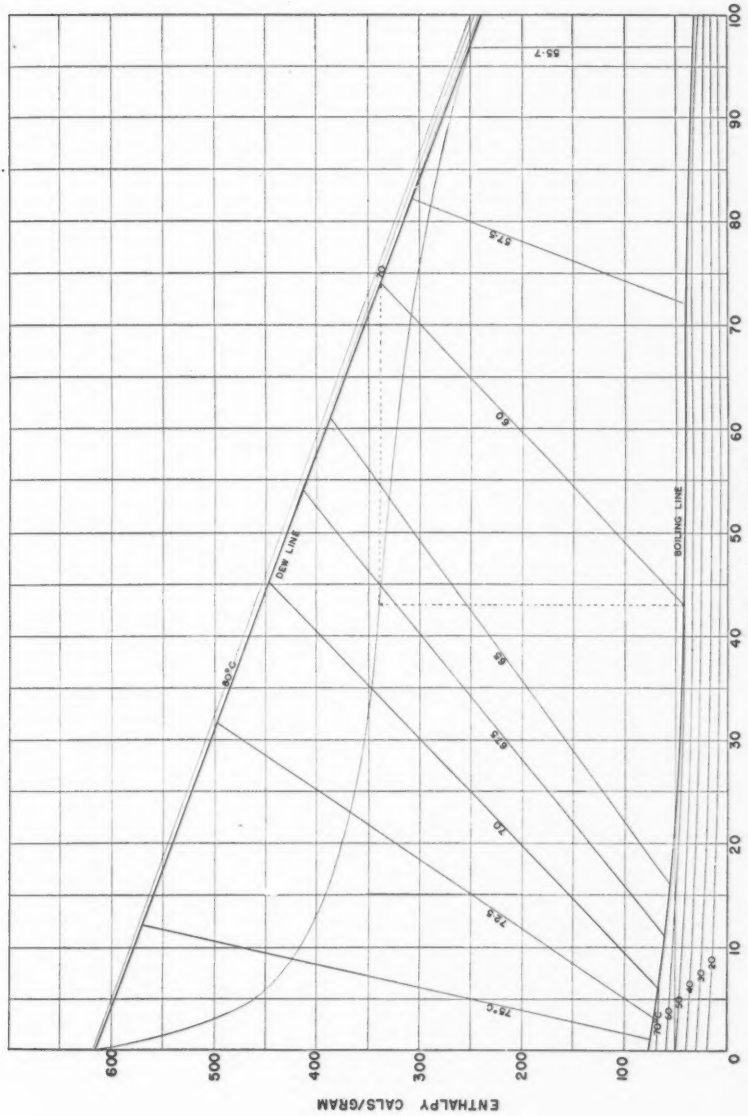

FIG. 6. Enthalpy–concentration diagram for ethanol–water mixtures at 300 mm.

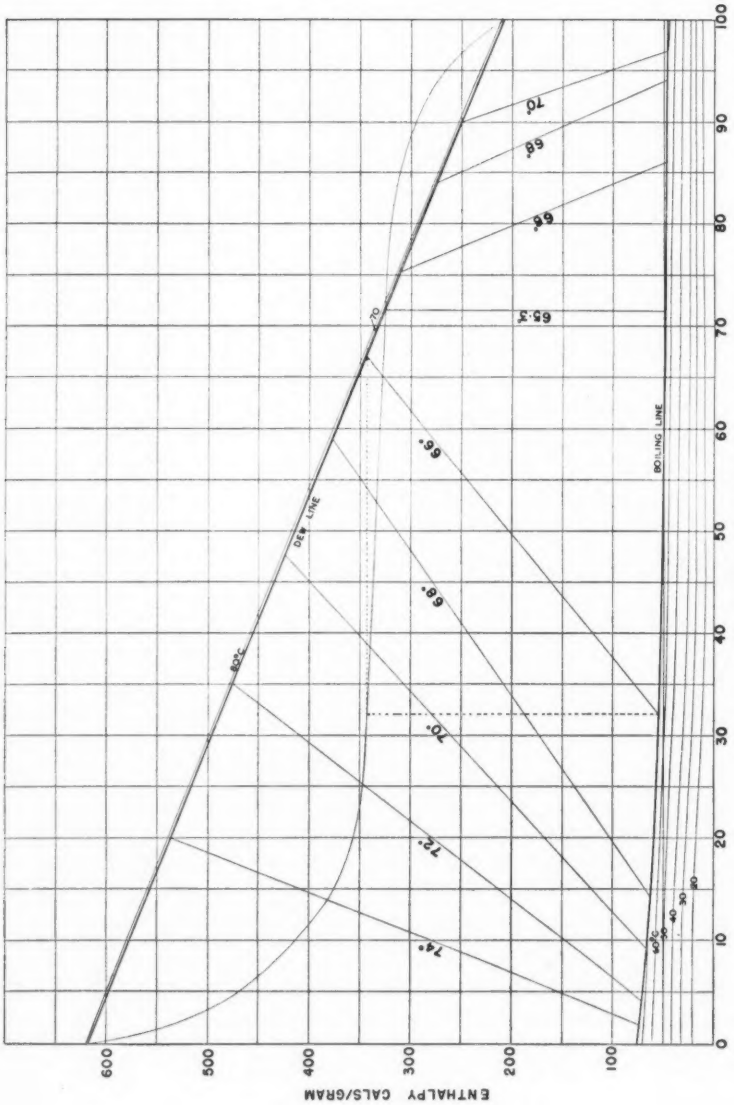

FIG. 7. Enthalpy–concentration diagram for *n*-propanol–water mixtures at 300 mm.

Former liquid–vapor studies in this department (13) for the three alcohol–water mixtures demonstrated the fact that the activity coefficients for the solute in dilute concentrations were considerably greater than one. This indicates great divergencies from ideality although heats of mixing show no such results.

Physically this may be visualized if one assumes for the moment that a molecule of water is one-half the size of an ethanol molecule. At the interface (gas–liquid) the addition of water to concentrated ethanol permits the replacement of one alcohol particle with two waters. As a result the concentration of water increases and the partial pressure of water molecules is greater than calculated by Raoult's law. An activity coefficient greater than one would be indicated.

Suppose also that alcohol is added to a water-rich mixture. At the interface one alcohol might be expected to replace two waters thus increasing the relative concentration of alcohol and the resultant partial pressure of the solute. Again an activity coefficient greater than one would be obtained for the ethanol in dilute concentration. It is important to note that this idea predicts positive activity coefficients for binary mixtures, if the molecules of one species are larger than those of the others and there is no heat of mixing.

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THE INFLUENCE OF OXYGEN, NITROGEN, AND CARBON ON THE MECHANICAL PROPERTIES AND MICROSTRUCTURE OF TITANIUM[1]

By O. Z. Rylski[2] and H. V. Kinsey[3]

ABSTRACT

It has been shown by this work that titanium containing as much as 0.25% oxygen, 0.15% carbon, and 0.08% nitrogen together with about 0.35% combined iron and aluminum will possess acceptable mechanical properties and that the maximum limit on these impurities before a serious deterioration of properties occurs is 0.32% oxygen, 0.18% carbon, 0.10% nitrogen, and 0.40% combined iron and aluminum. During this work, owing to the manner in which the alloys were prepared, it was not possible to vary the amount of one of these constituents without simultaneously varying the amounts of all of them.

INTRODUCTION

It is of fundamental importance to understand how variations in oxygen, nitrogen, and carbon content can influence the mechanical properties of titanium metal. Considerable information on this subject is to be found in the technical literature (1, 2, 3). Most of the work reported on in these papers dealt with alloys prepared from high purity titanium to which one or more of the above-named elements were added in controlled amounts. None of these papers contain data that could readily be directly applied to predicting quantitatively what happens to the mechanical properties of commercially pure titanium when its oxygen and nitrogen content is increased.

In the following investigation a series of "alloys" were prepared in which the oxygen, nitrogen, and carbon content varied between the following limits:

Oxygen — 0.11%–0.47%,
Nitrogen — 0.02%–0.16%,
Carbon — 0.07%–0.21%.

MATERIALS USED

To produce these alloys, titanium sponge produced by magnesium reduction of titanium tetrachloride (Kroll process) was blended in various proportions with titanium powder produced by the double reduction of titanium dioxide. The chemical analyses of these two types of titanium are given in Table I.

[1]*Manuscript received November 20, 1953.*
Published by permission of the Deputy Minister, Department of Mines and Technical Surveys, Ottawa, Canada.
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[3]*Head, Refractory Metals Section, Division of Physical Metallurgy, Mines Branch, Ottawa.*

TABLE I
CHEMICAL COMPOSITION OF THE MATERIALS USED

Material	N_2	O_2	H_2	C	Fe	Al	Mg	W
	Per cent							
Arc-melted Ti powder	0.16	0.47	0.017	0.25	0.338	0.316	0.005	0.05
Arc-melted Ti sponge	0.02	0.11	0.003	0.069	0.1	0.028	0.004	0.03

MELTING APPARATUS AND TECHNIQUE

The furnace used for melting is an inert atmosphere d-c. arc furnace using a water-cooled copper crucible. This furnace is similar to that described by Simmons *et al.* (4).

Evacuation to approximately 400 microns, followed by argon flushing, was carried out three times for each charge. A slight positive pressure (0.75 in. Hg) was maintained with a flow of argon of approximately 0.5 liter per minute. The crucible, electrode, and the cover were flushed with hot water (140°F.) prior to the last evacuation. Melting was done with a current of 600 amp. A current of 250 amp. was used at the start and at the end of melting.

Two 50 gm. buttons were melted for each composition. These buttons were crushed, mixed together, and remelted. The homogeneity of the final products was checked by hardness tests made on the entire area of 1/16 in. thick sheets rolled from the melted buttons. Hardness was checked at 10 mm. intervals. Fig. 3 shows the R_A hardness numbers as obtained for 70% Ti sponge – 30% Ti powder composition.

ROLLING

Ingots were hot rolled at 850°C. to approximately 1/4 in. thickness with 1/16 in. reduction in every pass. The ingots were reheated after each pass, so that the temperature of rolling was kept close to its upper limit. Approximately 40 to 50% total reduction was given to each ingot.

METALLOGRAPHIC EXAMINATION

For metallographic examination, samples from arc-melted buttons were cut from the edge, ground on the belt, and hand ground to 1/0, 2/0, 3/0 paper with normal precautions. Final polishing was done electrolytically. The following etching solution was used:

5 parts by volume of hydrofluoric acid (48%),
5 parts by volume of conc. nitric acid,
90 parts by volume of water.

CHEMICAL ANALYSES

All chemical analytical procedures used in this work are standard. Carbon was determined by the combustion method identical to that used for carbon

determination in steel. The nitrogen content was determined by a modified Kjeldahl process (5). Oxygen determinations were carried out by a vacuum fusion process. The apparatus and techniques used are similar to those developed by Walter (6).

RESULTS

The results of the chemical and gas analyses of the selected melts were found to be in close agreement with the values calculated from the original contents of the elements present in the two components used in the preparation of the mixtures. A typical example of this is given in Table II.

TABLE II

CALCULATED VS. DETERMINED OXYGEN CONTENT

Alloy components, per cent		Oxygen content, per cent	
Ti powder	Ti sponge	Determined	Calculated
0	100	0.11	
100	0	0.47	
30	70	0.225	0.216
60	40	0.335	0.325
75	25	0.38	0.38

This close agreement between obtained and calculated analysis would indicate that the gas content was not increased during melting and that the resulting melts were homogeneous. The calculated compositions of the various mixtures are given in Table III.

TABLE III

CALCULATED CHEMICAL ANALYSES OF THE METALS

Ti powder	Ti sponge	N_2	O_2	H_2	C	Remarks
Per cent		Per cent				
0	100	0.02*	0.11*	0.003*	0.069*	Al, Mg, Fe, and W contents in the mixtures were not analyzed. Original contents of these elements in Ti powder and Ti sponge are given in Table I.
15	85	0.041	0.16	0.005	0.096	
30	70	0.062	0.216	0.007	0.124	
45	55	0.083	0.27	0.009	0.151	
60	40	0.104	0.325	0.011	0.178	
75	25	0.125	0.380	0.013	0.205	
90	10	0.146	0.435	0.015	0.232	
100	0	0.16*	0.47*	0.017*	0.25*	

**These values obtained by actual analysis.*

Room temperature tensile, elongation, and hardness testing yielded the results shown in Table IV and Fig. 1. The design of the 0.25 in. diameter test bar used for this work is shown in Fig. 2.

TABLE IV
MECHANICAL PROPERTIES

Ti powder, %	Ti sponge, %	Hounsfield test bar, annealed				Hardness R_A	
		U.T.S., p.s.i.	Y.S., p.s.i.	Elong., %	Area red., %	Rolled	Annealed
0	100	72,600	64,500	33	53	54	53
15	85	106,200	105,200	28	37	61	61
30	70	131,800	130,000	15	15	64	59
45	55	142,500	139,800	10.5	10	66	66
60	40	147,000	145,600	10.5	9	68	67
75	25	130,500	..	Nil	Nil	69	69
90	10	100,800	..	Nil	Nil	71	71
100	0	88,900	..	Nil	Nil	72	72

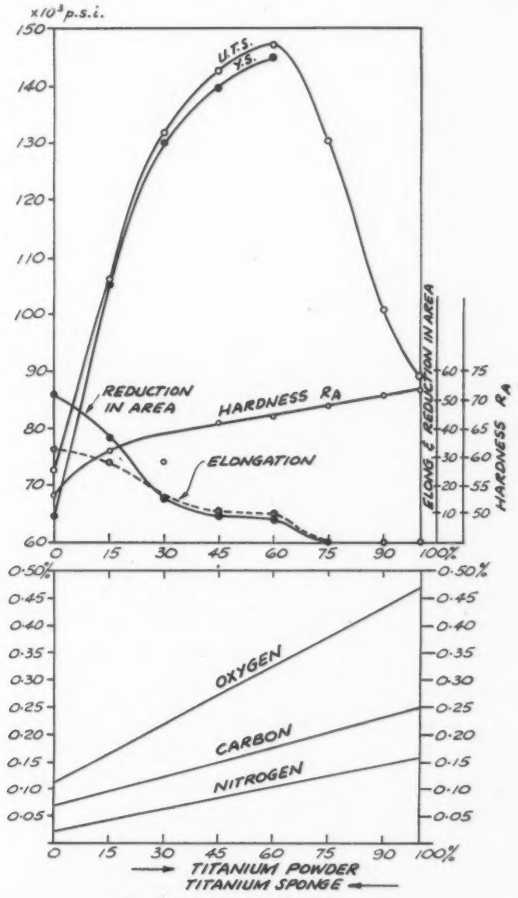

FIG. 1. Mechanical properties.

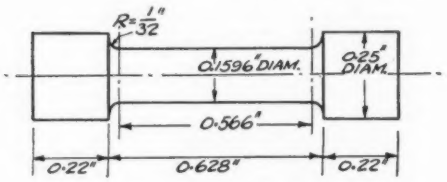

FIG. 2. Test bar Hounsfield tensometer.

Figs. 4 to 8 show the structure of the two components and some of the selected mixtures as revealed by metallographic examination.

DISCUSSION OF RESULTS

It is apparent that the effect of oxygen, nitrogen, and carbon on mechanical properties is of primary importance. Unfortunately, the method employed limited the range of this investigation to findings related to the combined effect of these embrittling elements in an a priori established range and relation. The contents of nitrogen, oxygen, and carbon were decreased proportionally and simultaneously with progressive additions of titanium sponge. The effect of varying the amount of one element at a time on mechanical properties was not established.

The curves in Fig. 1 show a very rapid change of mechanical properties up to and past a certain range of embrittling elements. The combined effect of 0.1% N_2, 0.32% O_2, and 0.18% C (in the presence of 0.4% combined Fe and Al) seems to be critical for the materials used. Past that range both strength and ductility drop very rapidly, though hardness shows only a slight increase.

The alloy having the following composition:

Oxygen	— 0.25%
Nitrogen	— 0.08%
Carbon	— 0.15%
Iron + aluminum	— 0.35%

possesses mechanical properties closely resembling those of some of the commercial titanium alloys.

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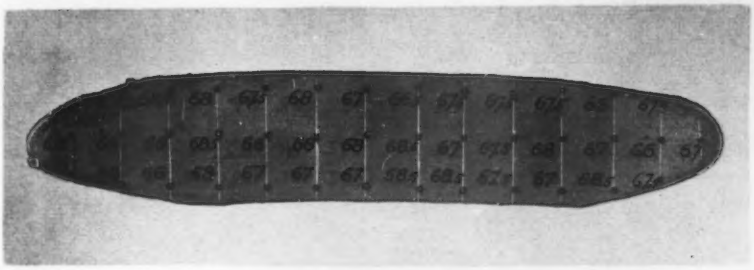
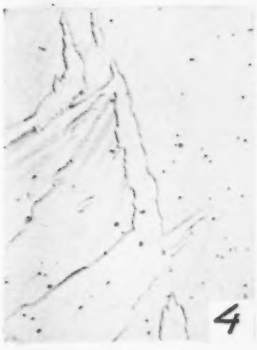
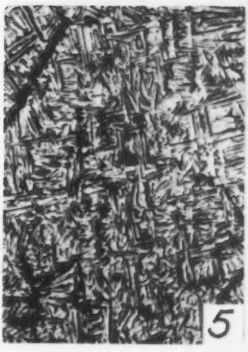
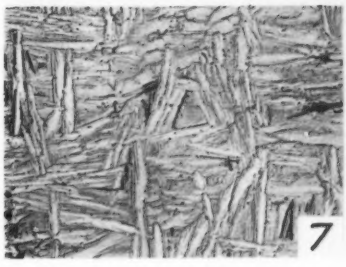
[NOTE: Figs. 3 to 8 follow.]









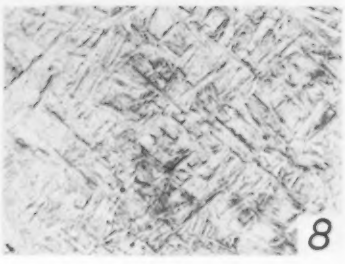


FIG. 3. (Top) Hardness test for 70% Ti sponge – 30% Ti powder.
FIG. 4. Arc-melted Ti sponge. × 300.
FIG. 5. Arc-melted Ti powder. × 300.
FIG. 6. 85% Ti sponge + 15% Ti powder. × 300.
FIG. 7. 40% Ti sponge + 60% Ti powder. × 300.
FIG. 8. 10% Ti sponge + 90% Ti powder. × 300

RESULTS AND CORRELATION

The results obtained are presented in Tables I–IV. Their graphical representation is given in Fig. 1 as a plot of $X_{CB}/(1 - X_{CB})$ versus $X_{CA}/(1 - X_{CA})$

TABLE I

EQUILIBRIUM DISTRIBUTION DATA FOR THE SYSTEM ACETIC ACID – WATER – CARBON TETRACHLORIDE

20°C.		25°C.		30°C.	
C_W, moles/liter	C_A, moles/liter	C_W, moles/liter	C_A, moles/liter	C_W, moles/liter	C_A, moles/liter
2.219	0.0636	1.342	0.0264	2.209	0.0676
1.823	0.0456	1.150	0.0202	1.541	0.0354
1.530	0.0330	0.986	0.0152	0.818	0.0115
1.266	0.0235	0.779	0.00976	0.428	0.00389
0.821	0.0104	0.536	0.00524	0.369	0.00315
0.658	0.00727	0.424	0.00344	0.339	0.00267
0.421	0.00323	0.290	0.00200	0.172	0.00092
0.336	0.00240	0.196	0.00107		
0.176	0.00087	0.138	0.00085		

TABLE II

EQUILIBRIUM DISTRIBUTION DATA FOR THE SYSTEM *n*-PROPIONIC ACID – WATER – CARBON TETRACHLORIDE

20°C.		25°C.		30°C.	
C_W, moles/liter	C_A, moles/liter	C_W, moles/liter	C_A, moles/liter	C_W, moles/liter	C_A, moles/liter
1.272	0.589	1.557	0.863	1.257	0.562
1.067	0.415	1.255	0.599	0.909	0.324
0.929	0.324	0.919	0.332	0.523	0.117
0.779	0.235	0.787	0.263	0.427	0.0802
0.525	0.115	0.550	0.133	0.257	0.0313
0.439	0.0817	0.456	0.0943	0.230	0.0258
0.290	0.0397	0.257	0.0325	0.123	0.0084
0.235	0.0248	0.206	0.0216	0.632	0.0029
0.124	0.0075	0.123	0.00756		

TABLE III

EQUILIBRIUM DISTRIBUTION DATA FOR THE SYSTEM *n*-BUTYRIC ACID – WATER – CARBON TETRACHLORIDE

20°C.		25°C.		30°C.	
C_W, moles/liter	C_A, moles/liter	C_W, moles/liter	C_A, moles/liter	C_W, moles/liter	C_A, moles/liter
0.384	1.079	0.341	0.881	0.381	1.080
0.340	0.856	0.310	0.733	0.301	0.702
0.305	0.703	0.279	0.601	0.200	0.324
0.269	0.552	0.205	0.335	0.117	0.118
0.202	0.321	0.150	0.185	0.110	0.104
0.176	0.244	0.119	0.117	0.0674	0.0413
0.119	0.116	0.085	0.065	0.0392	0.0155
0.0677	0.0408	0.0607	0.033		
0.0395	0.0142	0.0492	0.0219		

TABLE IV

EQUILIBRIUM DISTRIBUTION DATA FOR THE SYSTEM
n-VALERIC ACID – WATER – CARBON TETRACHLORIDE

20°C.		25°C.		30°C.	
C_W, moles/liter	C_A, moles/liter	C_W, moles/liter	C_A, moles/liter	C_W, moles/liter	C_A, moles/liter
0.0855	1.083	0.0865	1.052	0.0841	1.098
0.0757	0.904	0.0785	0.885	0.0689	0.753
0.0690	0.758	0.0641	0.612	0.0485	0.388
0.0624	0.617	0.0502	0.386	0.0315	0.166
0.0491	0.390	0.0385	0.231	0.0300	0.148
0.0436	0.310	0.0312	0.163	0.0204	0.0695
0.0319	0.167	0.0247	0.0988	0.0137	0.0319
0.0203	0.0704	0.0181	0.0548		
0.0137	0.0317	0.0089	0.0138		

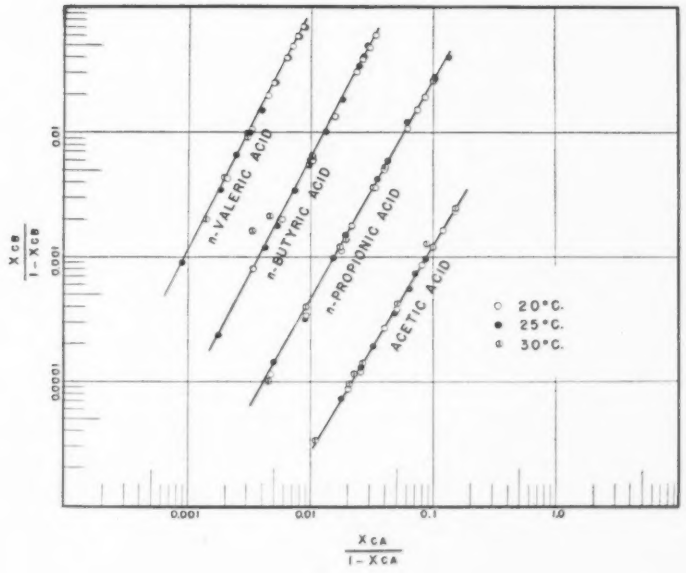


FIG. 1.

on log–log paper, X_{CB} and X_{CA} denoting the mole fractions of the distributing acid in the water layer and the carbon tetrachloride layer respectively. Since the variation was very small, the densities used in the calculations were those of water and carbon tetrachloride. Data on the distribution of each of the acids at 20°, 25°, and 30°C. are found to yield an identical straight line on the above graph. This indicates that, over the temperature range studied, the data can be interpolated for any desired temperature, for the different acids.

Each of these straight lines can be represented by the equation

$$\frac{X_{CB}}{1 - X_{CB}} = b \left(\frac{X_{CA}}{1 - X_{CA}} \right)^m$$

where m is the slope of the straight line pertaining to an acid, b is the intercept made by this line on the $X_{CB}/(1 - X_{CB})$ axis when $X_{CA}/(1 - X_{CA}) = 1$. The slopes of the different straight lines obtained for the different acids and the corresponding intercepts on the $X_{CB}/(1 - X_{CB})$ axis when $X_{CA}/(1 - X_{CA}) = 1$ are tabulated in Table V. From a plot of these values as a function of

TABLE V

Distributing acid	Molecular weight of distributing acid M	b	m
Acetic	60.05	0.058	1.65
n-Propionic	74.08	1.45	1.74
n-Butyric	88.10	24.2	1.81
n-Valeric	102.10	320	1.89

molecular weights of the corresponding distribution acids, as given in Figs. 2 and 3, the following correlations are established:

$$m = \frac{1}{1.01} \log \frac{M}{19.63}, \qquad b^{0.0594} = \frac{M}{72.46},$$

where M is the molecular weight of the concerned distributing acid.

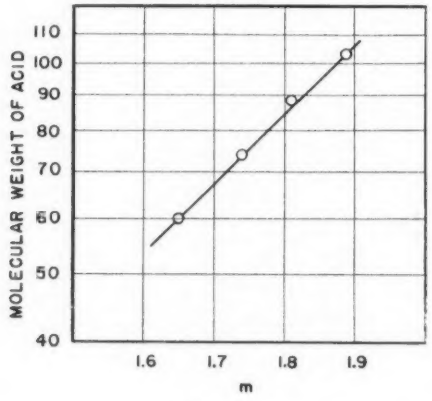


FIG. 2

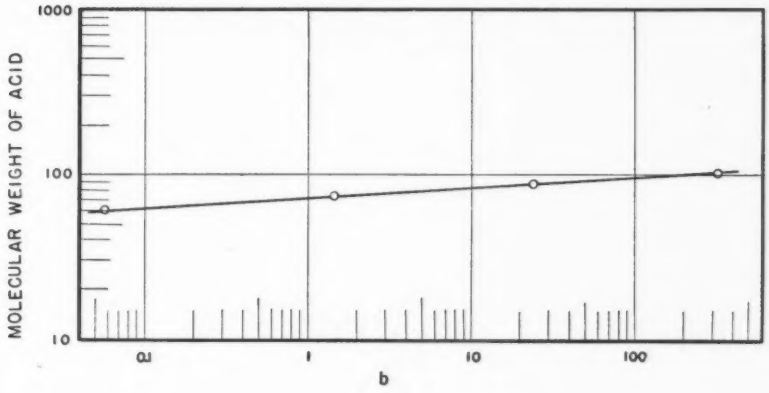


FIG. 3.

NOMENCLATURE

C_A : gram-moles of acid per liter of carbon tetrachloride phase.
C_W : gram-moles of acid per liter of water phase.
M : molecular weight of the distributing acid.
X_{CA} : mole fraction of the distributing acid in the carbon tetrachloride phase.
X_{CB} : mole fraction of the distributing acid in the water phase.
m : slopes of the lines in Fig. 1.
b : intercepts of the lines in Fig. 2, when $X_{CA}/(1 - X_{CA}) = 1$ on the $X_{CB}/(1 - X_{CB})$ axis.

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HUMIDIFICATION OF COLD STORAGES[1]

By C. P. Lentz

ABSTRACT

A system for humidifying cold storage rooms is described. Moisture removed from the room air during cooling by the refrigerant evaporator is absorbed by a nonfreezing aqueous ethylene glycol solution sprayed over the evaporator. The absorbed moisture is returned to the room from a continuously operating solution concentrator. Relative humidity varied linearly with rate of moisture return up to 100% relative humidity. Relative humidity at a constant rate of moisture return decreased with increasing spray solution concentration and increased with increasing rate of air circulation. Humidification from 62 to 100% relative humidity with the test room at 0° F. was found to increase the refrigeration load by one third and to double the power consumption. Changes in the design of the system which may reduce these increases are suggested.

INTRODUCTION

The storage life of many food products held in frozen storage is limited by surface desiccation or "freezer burn" caused by sublimation of ice at the surface of the product. Since the rate of sublimation is proportional to the difference in vapor pressure between the surface of the product (ice) and the storage atmosphere, surface desiccation cannot occur in a saturated atmosphere and will be retarded as the relative humidity approaches saturation. The necessity for very high relative humidities was indicated by Cook (2) who found that a relative humidity higher than 95% was required to store frozen poultry for more than a few months without serious freezer burn.

One of the main factors determining relative humidity is the temperature difference between cooling surface and room air; temperature differences which tend to produce relative humidities between 60 and 70% are commonly used. Relative humidities are often raised by increasing the cooling surface area or the room insulation thickness but both of these procedures have economic and practical limits. Surface desiccation can also be reduced by packaging, but this method is not applicable to many products. Other methods for reducing surface desiccation at frozen storage temperatures have therefore been investigated.

High humidities at subfreezing temperatures can be attained by reducing the rate of moisture condensation by the cooling system (5) or by direct humidification (3). Practical designs for high humidity systems and their efficiency and operating characteristics can only be determined by investigation. This paper deals with the direct humidification method. The objects of the investigation were:

1. To design a technically practical system for maintaining high relative humidity in cold storage rooms, and hence to indicate the type of equipment and controls which can be used.

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Contribution from the Division of Applied Biology, National Research Laboratories, Ottawa. Issued as Paper No. 299 of the Canadian Committee on Food Preservation and as N.R.C. No. 3297.

2. To determine the operating characteristics of the test system and the effects of varying some of the operating conditions within the range applicable to frozen food storage. (No detailed study of the heat and mass transfer performance of the evaporators was made.)

METHODS AND PROCEDURE

The direct humidification system operates essentially by recirculation of moisture. Water vapor removed from the air in passing through the cooling coils is absorbed by a nonfreezing solution sprayed over the coils, and returned to the room air from a continuously operating spray solution concentrator. Since the relative humidity depends on the rate of moisture addition to the room, any relative humidity up to saturation can be maintained by controlling the operation of the concentrator. If moisture is gained or lost by the system, periodic adjustment of the concentration of the spray solution may be necessary. Fig. 1 is a schematic sketch of the main working parts of the system.

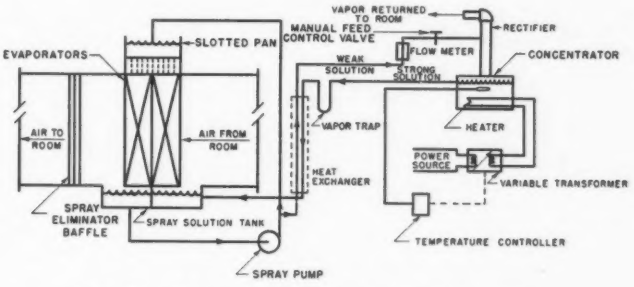

FIG. 1. Schematic sketch of humidification system.

Description of Test Room and Equipment

A room 20 ft. long, 10 ft. wide, and 10 ft. high insulated with 8 in. of rock wool and located in a space conditioned to 70° F. was used for the tests. Asphalt coated masonite was used as an outside vapor barrier on the walls and asphalt filled duplex kraft paper on the floor and ceiling. The evaporator, spray system, and a variable speed fan were located in a small, insulated, and vapor-sealed room adjoining the test room. Air from the cooling system entered the room through an opening at the top of one end wall and was returned through an opening at the bottom of the same wall. Water vapor was returned to the room from the concentrator through a short pipe entering the room in the center of one side wall. An 8 in. propeller fan dispersed the water vapor as it entered the room.

Ethylene glycol was selected as the freezing point depressant in the spray solution because of its relative cheapness, availability, large freezing point depression, and low vapor pressure. Some trouble was experienced from corrosion of iron and zinc during initial operation of the system. Borax, which was

used to inhibit the corrosion of iron at high temperatures, accelerated the corrosion of zinc at low temperatures and the inhibitor recommended for zinc did not protect the iron. The problem was solved by the use of protective coating on the zinc and substituting stainless steel for iron. Work has since been done on the corrosion properties of aqueous solutions of ethylene glycol (1).

The evaporators were wetted by gravity flow of the ethylene glycol solution through slots in a pan. This system was used in preference to a pressure spray because it did not cause fine droplets which would have been difficult to eliminate from the air stream.

The concentrator was designed for maximum concentration of the feed solution, and hence minimum feed rate and power consumption. The maximum strength of the solution was limited to that which would not freeze in the line returning to the spray tank. To further improve efficiency of operation, the feed and return lines formed a double pipe heat exchanger. A packed rectification column was used with the concentrator to reduce the ethylene glycol content of the vapor returned to the room to a level that would prevent condensation of ethylene glycol in the room. Its design was based on the assumption that the air leaving the spray chamber was saturated with ethylene glycol vapor.

The control system was designed for simplicity and cheapness. The strength of the solution leaving the concentrator was kept at the desired level by thermostatic modulation of electric heaters maintaining a constant boiling temperature in the concentrator. The amount of moisture returned to the room, and hence, the relative humidity in the room, was set by manual adjustment of the feed rate to the concentrator.

The room temperature was set by manual adjustment of electric reheat in the air leaving the evaporators, while the condensing unit operated continuously. This method of room temperature control gave more nearly constant room temperatures than "on–off" control would have given. In addition, the cooling system could be made to carry the heat load corresponding to a much larger room, increasing the relative accuracy of some of the measurements made during the tests.

Scope of Tests

The effects of rate of moisture circulation, concentration of spray solution, and air flow rate on relative humidity were examined in three series of tests:

1. Rate of moisture return to room (humidification rate) varied (60–100% R.H.), solution concentration and air flow rate constant (49% wt. conc., 1000 c.f.m.).

2. Solution concentration varied (43–56% wt. conc.), humidification and air flow rates constant (70% R.H., at 49% wt. conc., 1000 c.f.m.).

3. Air flow rate varied (600–1800 c.f.m.), humidification rate and solution concentration constant (70% R.H., at 1000 c.f.m., 49% wt. conc.).

Temperature conditions and the ranges of variables for the tests were selected to be in the range applicable to commercial storage practice.

Measurements

During each test 9 or 10 sets of measurements were made over a period of about three hours after equilibrium conditions had been reached. To avoid the effects of minor variations in the operation of the system, each test was repeated from three to five times on successive days and the results averaged.

Relative humidities were measured by the wet and dry bulb method and checked by the gravimetric method using chemical absorption. Initially, it was planned to use dewpoint measurement since the large change in dewpoint with relative humidity indicated greater accuracy than is normally possible using the wet and dry bulb method at temperatures well below freezing. Dewpoints measured with several modifications of a manually operated mirror type dewpoint apparatus, however, were not sharply enough defined to give an accuracy comparable with that of the wet bulb method. The wet bulb depression was measured with a series of 10 differentially connected fine wire copper–constantan thermocouple junctions. Preliminary tests showed that the effect of variations in air velocity was negligible for the conditions of the tests. Relative humidity was calculated with reference to the vapor pressure of ice since this is the datum of interest in the desiccation of frozen food products.

RESULTS AND DISCUSSION

Although every effort was made to conduct all experiments at a room temperature of 0° F., the temperature varied with humidification rate, fan power, and pump power. Hence all results were adjusted to make them comparable at a room temperature of 0° F. Since the adjustments were small (maximum: 3.5° F. at 102% R.H.) and the relations between the various temperatures were not changed, the validity of the results has not been affected. In the tests made with different spray solution concentrations and air velocities, a constant rate of humidification was used. Since the addition of a given amount of water vapor would have resulted in slightly higher dewpoints at 0° F. a secondary correction (maximum: 0.3° F.) was applied to the observed dewpoints.

Humidification Rate Tests

The relative humidity in the test room was found to vary linearly with the humidification rate (Figs. 2 and 3). During the first of these tests, although no moisture was being returned to the room, measurements made at the spray inlet and outlet showed that 0.2 grains of moisture per pound of dry air circulated was being absorbed by the spray. The amount remained relatively constant during repetitions of the test and was assumed to be the result of moisture leakage into the system. Operating conditions with no moisture leakage are shown by extrapolation in Figs. 2 and 3.

The differences in temperature between air, spray solution, and evaporators did not vary appreciably during the series of tests even though humidification caused a 19% increase in refrigeration load at 100% R.H. (Fig. 7). The constant temperature difference between room air and spray solution may

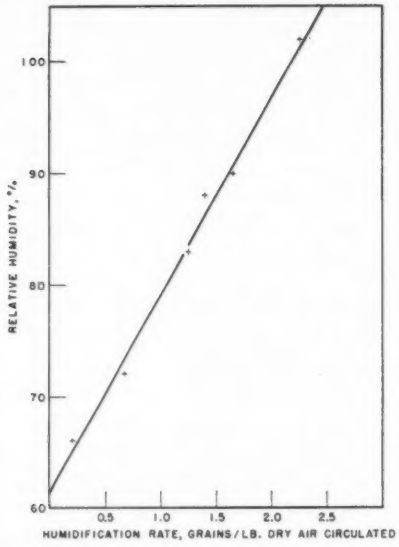

FIG. 2. Variation of relative humidity in test room with humidification rate.

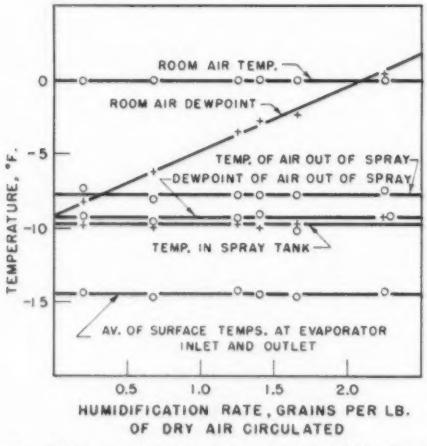

FIG. 3. Relation of temperatures to humidification rate.

be accounted for by the high coefficient of heat transfer for condensing water vapor. The constant difference between the temperatures of spray solution and evaporators (Fig. 3) was, however, unexpected and may indicate that the temperatures measured were not representative of temperatures at the wetted surface of the evaporators.

Although no published data are available to show the dehumidification caused by an ethylene glycol solution under the conditions of these tests,

extrapolation of published data (4) indicates that the equilibrium dewpoint of water vapor in contact with a 50% by weight ethylene glycol solution at −10° F. is about −20° F. In these tests, the dewpoint of the air leaving the spray was between −9 and −10° F. for all rates of humidification. This difference may be due to the dynamic rather than static conditions of the tests.

Room temperature and the difference between room and cooling surface temperatures have a marked effect on the amount of humidification necessary for a given increase in relative humidity but the effect of these factors can be calculated from psychrometric data, other conditions remaining constant. For example, raising the dewpoint from 0 to 10° F. requires 65% more moisture than raising it from −10 to 0° F., and raising it from −15 to 0° F. requires 150% more moisture than raising it from −5 to 0° F.

Tests made to determine what difficulties there might be in dispersing the water vapor entering the test room indicated that no appreciable condensation would occur if the vapor were added so that the humidified air stream was diluted by induced circulation before coming into contact with surfaces at the temperature of the room. This conclusion was confirmed in tests using the propeller fan to disperse the added water vapor and in tests where the vapor was introduced in the cold air stream entering the room.

Spray Concentration and Air Flow Rate Tests

The relative humidity in the test room at a fixed rate of humidification decreased as the concentration of the spray solution increased (Fig. 4). Increasing

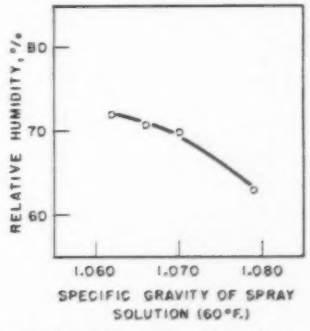

FIG. 4. Variation of relative humidity with solution concentration.

the solution concentration from 43% (sp. gr. 1.062 at 60° F.) to 56% (sp. gr. 1.079 at 60° F.) increased by 3° F. the dewpoint depression caused by the spray (Fig. 5). This rate of change is approximately that which would be expected from published data (4).

Although relative humidity increased markedly with air velocity (Fig. 6) the increase was not as great as would be expected from the increase in the spray temperature. This and the apparently poorer heat transfer from spray to cooling surface at the higher air velocities may indicate that less of the spray solution came in contact with coil surface at these air velocities.

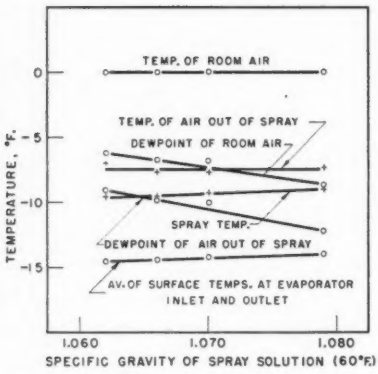

FIG. 5. Effect of spray solution concentration on temperatures.

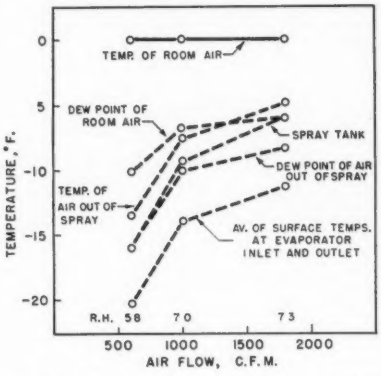

FIG. 6. Temperature conditions at three air flow rates.

Refrigeration and Power Load Increases

Maintenance of 100% relative humidity increased refrigeration and power loads by 34% and 92%, respectively, with the spray pump and the concentrator contributing about equally (Fig. 7). Refrigeration and power loads were

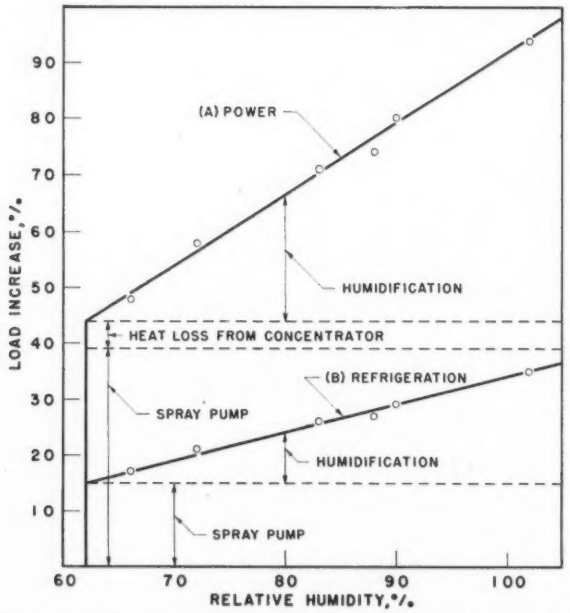

FIG. 7. (A) Power load increase with increasing relative humidity.
(B) Refrigeration load increase with increasing relative humidity.

Notes.—(1) Refrigeration load with humidification equipment not operating, 10,000 B.t.u./hr. (2) Power load with humidification equipment not operating, 6,000 B.t.u./hr. (3) Compressor power calculated on basis of 2.5 h.p./ton of refrigeration. (4) Spray pump power, 1500 B.t.u./hr. (5) Fan power, 700 B.t.u./hr.

linearly related to relative humidity. The increase in both refrigeration and power loads caused by the latent heat load due to humidification could be reduced by lowering the room temperature or by decreasing the temperature difference between the room and the cooling surface. The first method would not be satisfactory for many types of equipment because increase in external heat load and lowered compressor performance would more than offset the reduction in latent heat load. The second method would be more practical since the latent heat load is almost proportional to temperature difference.

Observation of the test system in operation indicated that the pump load could be considerably reduced by improved design of the evaporators and spray system. The evaporators in the test system were not designed for gravity flow wetting (a pressure spray was initially planned) and keeping them clear of frost required the pumping of much more liquid than should be necessary with specially designed evaporators. The large amount of liquid pumped did improve heat transfer, although not as much as it would have if the falling drops of solution had been smaller. A better system may therefore be one in which the evaporators are submerged in the spray solution and the air is cooled by sprayed droplets just large enough to be easily eliminated from the air stream.

CONCLUSION

These tests have shown that only relatively simple equipment is required to maintain a cold room at any desired level of humidity above that normally obtained. Although the increase in operating cost required for this method of humidification is comparatively large, the importance of this increase depends on many factors including the value of storing a product at a satisfactory level of humidity and the proportion of the total cost of storage represented by operating costs. It should be noted that part of the increased cost of operation of this system is offset by the increased efficiency of frost-free evaporators.

As relative humidity for the storage of frozen food products is increased, several additional factors may become increasingly important. Two of these are velocity of air movement and absorption of water vapor by packaging materials. Both of these factors will be examined in the study of the jacketed type storage room now under way in these laboratories.

ACKNOWLEDGMENT

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GRAPHICAL DETERMINATION OF MAXIMUM CAPACITY OF A WASHING FILTER PRESS[1]

By Norman Epstein

ABSTRACT

A graphical method is presented for determining the cycle corresponding to maximum daily capacity of a washing filter, provided the wash fluid is of the same density and viscosity as the filtrate. The reliability of the answer depends only upon the accuracy of the operating data.

Standard textbooks in chemical engineering (1, 2) give a simple graphical procedure for determining the filtration cycle corresponding to the maximum over-all capacity of a nonwashing filter press. This procedure involves merely laying off the horizontal distance OP, equal to the cleaning-and-reassembly time θ_c, to the left of the origin of the V–θ_f filtration curve, and drawing the straight line tangent from P to this curve. The point of tangency then represents the filtration cutoff point for a maximum capacity cycle. The same method can be applied to a washing filter only if the washing time is arbitrarily fixed at some given value which is independent of the amount of filtration previously carried on, by simply adding this fixed time θ_w to θ_c and marking off the intercept OP as equal to $\theta_w + \theta_c$, rather than θ_c alone. This, however, does not correspond to practical operation, where the volume of wash fluid used and therefore the washing time depend upon the amount of filter cake previously deposited, a quantity which is proportional to the amount of filtrate collected.

For a given degree of washing, the required wash fluid volume V_w bears a fixed ratio r to the filtration volume V, i.e.,

$$V_w/V = r. \qquad [1]$$

If the wash fluid has the same density and viscosity as the filtrate, and the washing is performed at constant pressure,

$$V_w/\theta_w = c(dV/d\theta)_F, \qquad [2]$$

where the constant c depends on the washing pressure and the path followed by the wash fluid. Combining equations [1] and [2],

$$(dV/d\theta)_F\theta_w = (r/c)V. \qquad [3]$$

The graphical solution for a washing filter is illustrated in Fig. 1, where the V–θ_f line represents the best curve through the operating data for a given filter. The plot of V vs. $(\theta_f + \theta_w)$ may be obtained from this curve by the

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Contribution from the University of British Columbia, Vancouver, B.C.

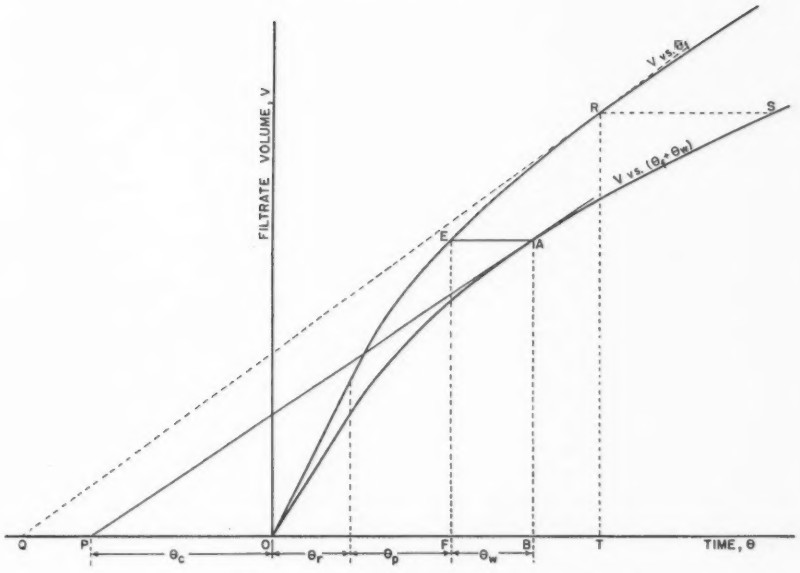

FIG. 1. Analysis of filtration cycle.

following application of equation [3]. Suppose filtration were to cease at point R, then

$$[4] \qquad (dV/d\theta)_F = RT/TQ = V/TQ,$$

where RQ is tangential to the V–θ_f curve at R. For any point R on the V–θ_f curve, a corresponding point S on the V–$(\theta_f + \theta_w)$ curve must be such that

$$[5] \qquad RS = \theta_w.$$

Combination of equations [3], [4], and [5] leads to

$$[6] \qquad RS = (r/c)TQ,$$

thus fixing the point S. Using this relationship, the entire curve of V vs. $(\theta_f+\theta_w)$ may be plotted, given c, r, and the V–θ_f curve. The over-all average filtration rate $V/(\theta_c + \theta_f + \theta_w)$, corresponding to maximum capacity, is then given by AB/PB, where A is the point of tangency of PA to the lower curve. The horizontal line EA between curves represents the required washing time, and the distance OF the filtration time, for maximum capacity operation.

Like the nonwashing method, this procedure is applicable whether or not a constant-rate filtration period is included in the cycle. Both methods do not require the use of theoretical filtration equations, and depend for their accuracy only on the validity of the operating V–θ data. Such data, including the value of the constant c in equation [2], are most reliably obtained from plant-scale

tests. In the absence of washing tests, the constant c may be taken as unity for simple displacement washing, and approximately one quarter for "through-washing" in a plate-and-frame press, provided the common practice of washing at the same pressure as the final filtration is followed. The ratio r of wash fluid to filtrate is fixed by the degree of washing desired.

NOTATION

θ = time.
θ_c = time for cleaning and reassembling filter press.
θ_f = filtration time.
θ_r = constant-rate filtration time.
θ_p = constant-pressure filtration time for maximum capacity cycle.
θ_w = washing time.
V = volume of filtrate.
V_w = volume of wash fluid.
$(dV/d\theta)_F$ = final filtration rate.
c = ratio of washing rate to final filtration rate.
r = ratio of wash fluid volume to filtrate volume.

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THE MICROSTRUCTURES OF VARIOUS GRADES OF TITANIUM AND THEIR RATES OF FORMATION[1]

By W. D. Bennett[2]

ABSTRACT

Typical microstructures of various grades of pure and impure titanium are given and some conclusions drawn on the effects of purity and mechanical and thermal treatments on their rates of formation.

Although a considerable amount of work has been done on the metallography and properties of commercial titanium (1, 3, 5) there seems to be very little in the literature on the structures of very pure iodide titanium and on the nature of the martensitic transformation which takes place when small impurities are present. The following account of work on arc-melted DuPont titanium, induction-melted DuPont titanium (containing carbides), arc-melted iodide titanium, and commercial Ti75A (obtained from the Titanium Metals Corporation of America) shows how the rates of formation of both the martensitic type acicular structure and the equiaxed structure are closely related to the purity and the state of internal stress of the metal.

SPECIMEN PREPARATION

Specimens were prepared by polishing mechanically down to 3/0 paper, followed by electrolytic polishing. The electrolyte used was that recommended by Jaquet (4): it consists of 795 cc. of acetic anhydride, 185 cc. of perchloric acid, and 48 cc. of water. Best polishing conditions were found to be obtained with a current density of 0.2 to 0.3 amp./sq. cm. for successive periods not exceeding 45–60 sec. each. Excessive heating will result in a poor polish. This electrolyte is quite safe, although care should be taken, in making it up, to mix the components slowly and in the sequence listed above. An effective etchant was found to be 12 cc. nitric acid, 1 cc. hydrofluoric acid, and 87 cc. water for 15–30 sec.

All specimens used were between $\frac{1}{4}$ and $\frac{1}{2}$ cc. in volume and, except where otherwise stated, were vacuum sealed in quartz capsules for heat treatment. Mounting was not done in bakelite or other plastics, for fear of introducing excessive twinning.

1. *DuPont Titanium Melted in Graphite Under a Vacuum (Ti-1)*

The chemical analysis of this metal after melting was: carbon, 0.41%; nitrogen, 0.02%; oxygen, 0.13% to 0.23%; iron, 0.10%.

Four identical specimens, initially in the equiaxed alpha condition, were heated for a hour at 880° C., 900° C., 930° C., and 980° C. respectively, and water quenched, the quartz containers being shattered under water.

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[2] *Research Metallurgist.*

Figs. 1 to 4 illustrate the microstructures. When quenching is from the beta region (i.e. as in Fig. 4) a type of martensitic structure is formed, often described as Widmanstatten, "basket work", or acicular.[3] When quenching is from the two-phase alpha plus beta region, both acicular and equiaxed alpha appear. Heating in the alpha region at 880° C. produces a completely equiaxed alpha structure. In all cases the carbides appear as long stringers.

These microstructures indicate that this grade of titanium has a two-phase region between 880° C. and 980° C. The small grain size and the ease with which the acicular can be recrystallized into equiaxed alpha (one hour at 870° C.) are characteristic features of titanium containing carbon.

2. *Iodide Titanium Arc-melted Under Argon (Ti-3)*

The metal was of very high purity, the maximum contamination being: manganese, 0.015%; iron, 0.006%; aluminum, 0.01%.

One of the first and unmistakable features of the high purity titanium was the ease with which twinning took place with the slightest deformation. This meant that the specimens could not be constrained in any way and that the electrolytic polishing had to be deep enough to remove the surface layer, otherwise twins formed adjacent to the mechanical scratches.

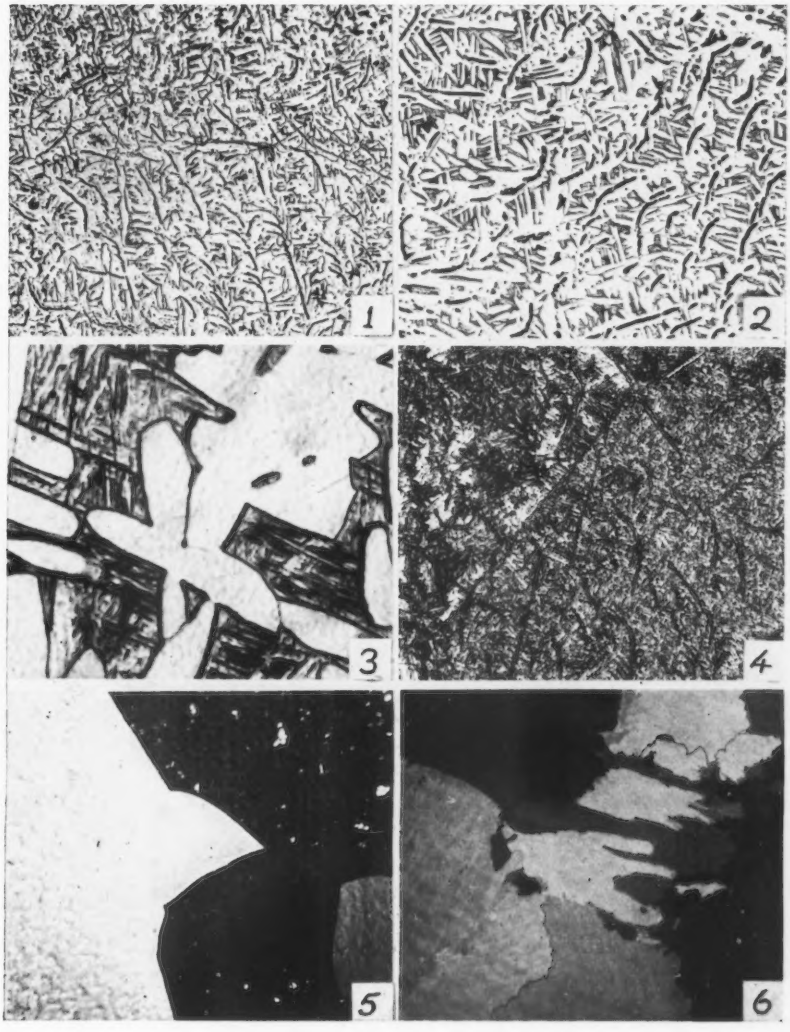
Two photomicrographs, Figs. 5 and 6, illustrate the differences which exist between specimens quenched from the alpha and the beta phases. The grain boundaries in the metal quenched from the beta phase are serrated, whereas those in the metal heated below the transformation temperature are sharp and smooth. The two photomicrographs were taken under polarized light, as this type of illumination enables one on closer examination to detect a parallel lamina-type structure within the grains of the beta quenched metal. These laminae or needles appear to be related to the serrated grain boundaries. A similar effect has been described by Holden, Ogden, and Jaffee (2).

It was not possible to detect any signs of a two-phase region even though a closely grouped series of quenching temperatures was used. This result is not surprising, considering the high purity of the metal.

Fig. No.	Description	Etchant	Magnification
1	Ti-1. Equiaxed alpha and carbide stringers. Water quenched after one hour at 880° C. Similar to "as-cast".	12 cc. HNO_3 1 cc. HF 87 cc. H_2O	× 66
2	Ti-1. Equiaxed alpha plus transformed beta and carbide stringers. Water quenched after one hour at 930° C.	ditto	× 66
3	Ti-1. Equiaxed alpha plus transformed beta (approximately 50%). Water quenched after one hour at 980° C.	ditto	×666
4	Ti-1. Transformed beta and carbide stringers. Water quenched after one hour at 980° C.	ditto	× 66
5	Iodide titanium. Equiaxed alpha. Water quenched after one hour at 850° C.	none[4]	× 66
6	Iodide titanium. Serrated alpha. Water quenched after ½ hr. at 1000° C.	none[4]	× 66

[3] *Acicular alpha, being a martensitic type of structure, is sometimes referred to as transformed beta.*

[4] *Viewed with polarized light.*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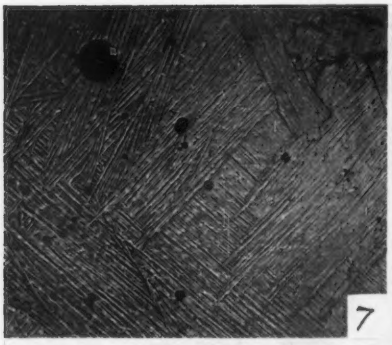
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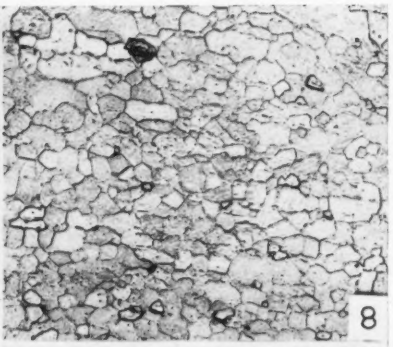
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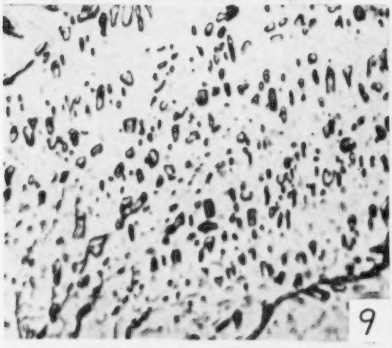
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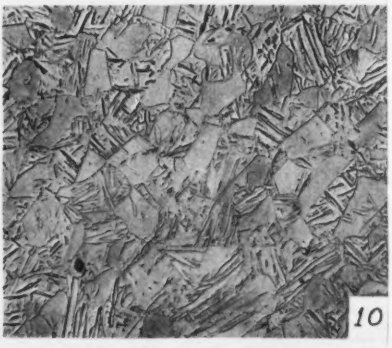
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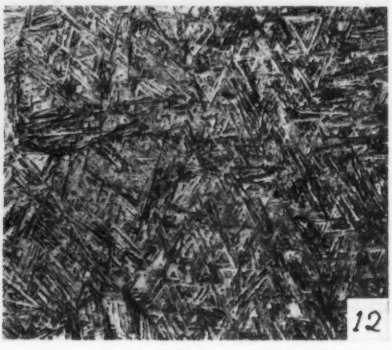
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3. *DuPont Titanium Arc-melted Under Argon (Ti-2)*

The chemical analysis after melting was: nitrogen, 0.01%; oxygen, 0.19%; hydrogen, 0.005%; iron, 0.10%; aluminum, 0.10%; carbon, nil.

The carbon-free material behaves quite differently from the Ti-1, and the microstructures are somewhat similar to those given by Craighead (1) for his Process A metal. In the "as-cast" condition the metal is characterized by a form of parallel acicular structure, which is illustrated in Fig. 7. Quenching from the beta region produces the typical Widmanstatten, "basket work" type of acicular structure (Fig. 12) very similar to that shown in Fig. 4 for Ti-1. It is in attempting to produce a uniform equiaxed alpha structure that difficulty is experienced in eliminating all traces of the original as-cast acicular structure. Heating for one hour in the alpha region at 880° C. is insufficient. Even 48 hr. at this temperature does not remove completely all traces of the original structure.

The introduction of internal stresses in the form of 50% reduction by cold work at room temperature has the effect of accelerating the recrystallization process. When this cold work is followed by 18 hr. at 780° C., a complete and uniformly equiaxed structure is formed (Fig. 8).

In examining this equiaxed structure at high magnification there are regions where small islands appear within the grains. These might be another phase (possibly titanium hydride) and are labelled "X" phase in Fig. 9.

When a 100% equiaxed structure is heated at 900° C. for one hour and water quenched, mixed regions of acicular and equiaxed alpha are produced (Fig. 10) similar to those shown in Fig. 3 for Ti-1.

4. *The Effects of Quenching Rates on the Type of Martensitic Structure*

Figs. 11 and 12 show microstructures of two identical specimens of arc-melted DuPont titanium after the specimens had been heated for one hour *in vacuo* at 980° C. The specimen shown in Fig. 11 was allowed to air cool in the quartz capsule, but the one in Fig. 12 was water quenched with a simultaneous breaking of the capsule.

Although the air-cooled specimen cooled at about 540° C./min., there is quite a difference between its structure and that of the more rapidly quenched specimen. Both are acicular but one is of the parallel type and the other the "basket work" type of structure.

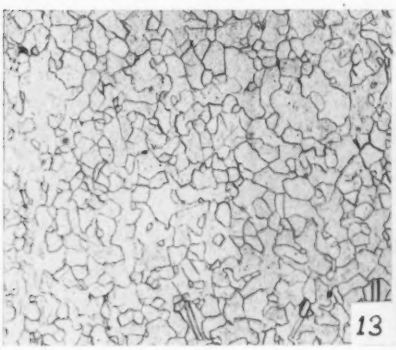
Fig. No.	Description	Etchant	Magnification
7	Ti-2. Acicular alpha "as-cast".	12 cc. HNO_3 1 cc. HF 87 cc. H_2O	×100
8	Ti-2. Equiaxed alpha. Cold worked. 18 hr. at 780° C. and water quenched.	ditto	×133
9	Ti-2. As in Fig. 8, but higher magnification, showing "X" phase.	ditto	×666
10	Ti-2. Equiaxed alpha plus transformed beta. Specimen shown in Fig. 8 heated for one hour at 900° C. and water quenched.	ditto	×333
11	Ti-2. Air cooled in sealed quartz capsule after one hour at 980° C.	ditto	×100
12	Ti-2. As in Fig. 11 but water quenched.	ditto	×100

5. *Ti75A Supplied by the Titanium Metals Corporation of America in $\frac{1}{4}$ In. Bar Stock*

A nominal composition is given by the manufacturers: iron, 0.10%; nitrogen, 0.02%; oxygen, 0.10%; carbon, less than 0.04%.

The microstructures for this metal were very similar to those obtained with the arc-melted DuPont titanium (Ti-2). Fig. 13 is shown to illustrate the microstructure of the metal as received from the producers. It shows that the bar stock was annealed after rolling, as the structure is completely equiaxed.

An interesting example of the surface contamination of titanium with oxygen and nitrogen was obtained in heating a specimen for one hour at 980° C. in air and water quenching (Fig. 14). Sufficient oxygen and nitrogen has been



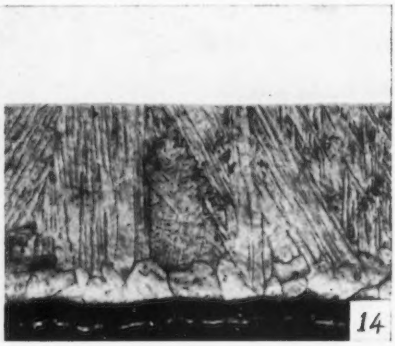


Fig. No.	Description	Etchant	Magnification
13	Ti75A. Equiaxed alpha. As received.	12 cc. HNO_3 1 cc. HF 87 cc. H_2O	×100
14	Ti75A. Edge effect due to absorption of oxygen and nitrogen. 980° C. for one hour in air and water quenched. (Note that alpha titanium is retained on the surface.)	ditto	×300

absorbed by the metal at the surface to raise its alpha–beta transus above the heating temperature. The thickness of this oxygen plus nitrogen enriched layer is indicated by the extent of the equiaxed alpha titanium at the surface. The main body of the metal was heated above the transformation temperature in the beta phase and has transformed isothermally to acicular alpha.

CONCLUSIONS

In all commercial grades of titanium studied in this investigation, a martensitic type of structure is produced when quenching is from the beta phase. There is also a similar structure in iodide titanium. The size of needles formed in this way is related to the purity and increases with decreasing amounts of oxygen and nitrogen.

The presence of a two phase temperature region, where the alpha and beta phases coexist in equilibrium, is confirmed for the commercial grades of

titanium. Specimens, initially in the equiaxed alpha state, when heated in this limited intermediate temperature range and quenched, show mixed regions of acicular and equiaxed alpha.

For the arc-melted DuPont metal and the Ti75A, either prolonged heating (three days or more) or a combination of cold work and short heating period in the high temperature portion of the alpha region was necessary to change the martensitic structure into purely equiaxed structure. (In investigating the alpha plus beta regions of an alloy phase diagram which behaved in this way it would be important to obtain a 100% equiaxed alpha structure before increasing the temperature to a value in the mixed phase region from which the quenching was to be done). The iodide titanium and the carbon-containing titanium, on the contrary, could be readily recrystallized into the pure equiaxed structure by short-period heats in the alpha region.

Quenching iodide titanium from the beta phase gives serrated grain boundaries and some indication of parallel laminae inside the main crystallites. It may be that the speed with which equiaxed alpha forms in the pure material forestalls the formation of an acicular type of structure and that the speed of quenching should be increased with increasing purity, if a martensitic structure is to be formed.

Qualitative support of this is given by Figs. 11 and 12; the structure shown in Fig. 11 is somewhat similar to the beta quenched iodide titanium structure and is characteristic of retarded quenching rates. Presumably an infinite speed of quenching is required at the ideal purity of 100% titanium, where it may be impossible to produce any form of martensitic structure. A closer and more precise investigation of the effects of quenching rates on the structure of high purity titanium would be of interest.

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PREPARATION OF STANDARD FILMS OF CRYSTALLINE *p–p'*-DDT FOR LABORATORY INVESTIGATION BY SUBLIMATION[1]

By R. J. Cvetanović[2] and D. P. Pielou[3]

ABSTRACT

A sublimation technique is described for the deposition of thin films of DDT crystals on glass. These deposits contain a prescribed amount in a given area.

INTRODUCTION

Work in progress on the selective breeding of a DDT-resistant strain of *Macrocentrus ancylivorus* Rohw., a parasite of the oriental fruit moth, had as a prime requisite the need for a test surface of pure *p–p'*-DDT that could be quickly and exactly reproducible to given specifications. These specifications were that the DDT film be wholly crystalline, uniformly dense, and of stated quantity in a defined area on glass.

Various techniques that had been developed met some, but not all, of these requirements. Direct deposition from solution often results in a deposition of supercooled globules, which partially crystallize after prolonged standing or when a test insect walks on them (Parkin and Green (9)). Crystallization was also induced, by the movement of an insect, in the methods described by Browning *et al.* (2) and by Picard and Kearns (11), and, although quick and convenient, these methods were ruled out for our requirements. The possibility that the deposited globules might retain minute quantities of the solvent that might modify toxicity (Musgrave (8), Deffner and Augustides (4)) was considered serious. Patton and Sarkaria (10) describe a method of depositing crystalline DDT by mixing dry DDT crystals with starch as a carrier, dispersing the mixture from a dust tower, and washing the starch away from the plates upon which the mixture has fallen. This method was considered but was ruled out as too awkward for regular daily use; moreover, it would be difficult to deposit repeatedly specified amounts in a circumscribed area. The spray tower method (15) gives good films, but very close attention to the mechanical operation and frequent quantitative determination of the deposits are essential for the repeated preparation of similar test surfaces.

Two methods were devised at the Belleville laboratory. The first, already described (Pielou (12), Pielou and Glasser (13)), satisfied all requirements, but the DDT was deposited on glass in a very thin film (0.1 to 0.2 μ thick) of inert celloidin. This method, however, is extremely rapid and convenient and is the one used in selection work on *M. ancylivorus* (Pielou and Glasser (13)), many thousands of films having been made.

Development of the other method was commenced at the same time and is described in this paper.

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[3]*Entomology Laboratory, Belleville, Ont. Now at Entomology Laboratory, Summerland, B.C.*

TECHNIQUE

The principle is to vaporize a known amount of DDT from a heated hemispherical dish, and to deposit the DDT on a cooled flat glass plate that also acts as a close fitting lid for the evaporating dish. The apparatus (Fig. 1) consists essentially of a solid cube of cast aluminum, approximately 6 in. high, which is heated electrically and thermostatically controlled. The hemispherical

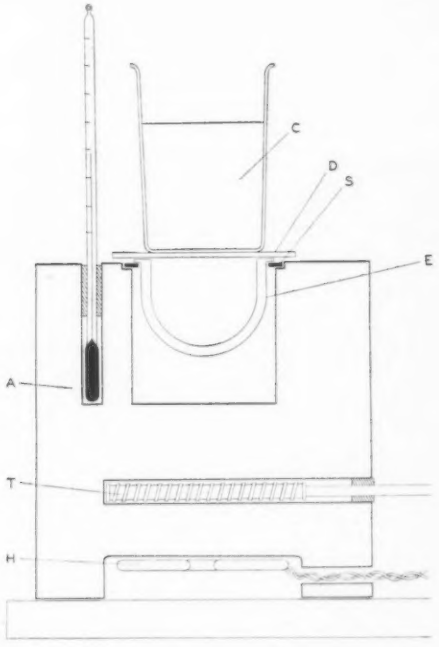


FIG. 1. Cross section of apparatus. *A*, aluminum heating block; *C*, coolant and weight holding down deposit slide (*D*, a lantern cover glass); *E*, evaporating dish; *H*, heater; *S*, support ring for evaporating dish; *T*, thermostat element.

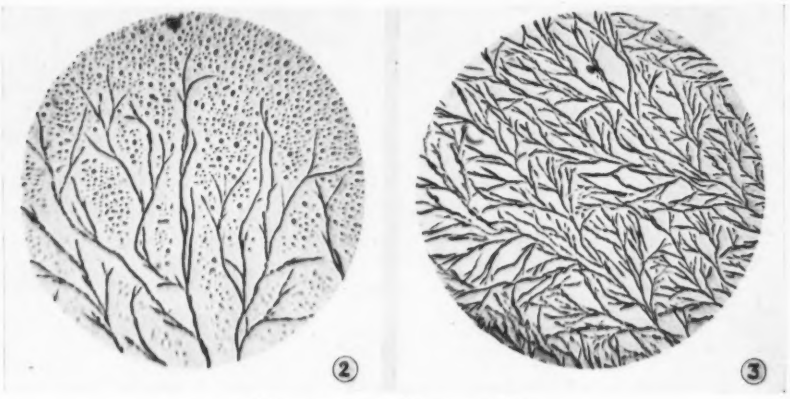
glass evaporating dish has an internal diameter of 2 in. and has a lipped rim that is ground flat. It rests in the heating well of the block and is supported on an annular ring that fits in a small recess at the top of the well. A lantern slide cover glass, size $3\frac{1}{4} \times 3\frac{1}{4}$ in., lies flat on the ground glass rim of the dish and is held down by a copper beaker filled with cold water.

In use, a known amount of pure *p*–*p*′-DDT in acetone is added to the dish. The solvent is allowed to evaporate and the dish is thoroughly dried in a desiccator. The glass slide is cleaned very thoroughly with a solvent and lens paper; a thorough cleaning is essential for uniform deposits. The cleaned glass slide is also placed in a desiccator before use as all trace of moisture must be removed; moisture interferes with crystallization and results in uneven deposits.

With the thermostat set to give a block temperature of 160° C., the dish is removed from the desiccator and is placed on the support ring of the heating well. The clean glass plate is placed in position and the copper beaker of coolant put on top. Deposition of the DDT is completed in a short time through evaporation and subsequent condensation.

CRYSTALLIZATION OF THE DEPOSITS

The DDT is deposited in the form of minute supercooled globules that tend to crystallize into a branching arrangement of microcrystals (Fig. 2). This tendency is greater when the globules are closer together, and crystallization takes place readily in deposits containing larger amounts of DDT per unit area (Fig. 3). Deposits containing amounts of DDT suitable for most experi-



Microscope magnification ×300.
FIG. 2. Supercooled globules of DDT in the process of crystallization.
FIG. 3. Crystallized deposit of DDT.

mental purposes crystallized in one to two days. Touching the surface with the tip of a glass rod, drawn out to a fine point, assists in inducing well-spaced centers of crystallization. During the crystallization period the glass plates should be left in a desiccating chamber.

In the evaluation of insecticidal action of these very thin films a point to remember is that, for a given amount of DDT per unit area, larger crystals cover a lesser amount of the total area than smaller crystals. In the former case small insects walking on the films spend a greater period of time with their tarsi in contact with the plain glass—the spaces between the crystals—than in the latter. The *percentage coverage of the deposit* for a given concentration of material per unit area depends on a variety of factors, e.g., temperature evaporation surface, temperature condensation surface, number of artificially induced centers of crystallization. These must be standardized to suit the particular insects being investigated.

TEMPERATURE RANGE

At higher temperatures *p–p'*-DDT decomposes with evolution of hydrogen chloride. This decomposition is strongly catalyzed by certain substances even when present in very small quantities (Fleck and Haller (5), Flenner (6)).

Balaban and Sutcliffe (1) have defined the decomposition points of samples of DDT as the temperature at which gas, drawn from a tube in which a small sample was heated at a constant rate of increase in temperature, formed a definite turbidity in a 1% solution of silver nitrate. They recorded a decomposition point of 195° C. Scholefield *et al.* (14) state that there is a very slight evolution of hydrogen chloride even at the melting point of the compound, and that it becomes rapid in the neighborhood of 200° C. On the other hand, Flenner (6) found that a highly purified sample of *p–p'*-DDT evolved no hydrogen chloride in 24 hr. at 115° C. Similarly, Gunther (7) could not observe any decomposition when heating DDT for 24 to 48 hr. at 110° C. in a sealed test tube in the presence of dry air. Cutkomp (3), however, showed that boiling, autoclaving, or heating in water above 90° C. decomposes dilute aqueous dispersions.

For the present work the thermal stability of pure *p–p'*-DDT (m.p. 108.5° C.) has been explored by heating the compound in sealed ampoules of resistant glass for 30 min. at various temperatures. The ampoules contained about 0.7 gm. of the compound and after exposure they were rapidly cooled to room temperature and then broken at the bottom of a narrow glass cylinder containing 100 ml. of distilled water. The change in hydrogen ion concentration of the distilled water following this operation and resulting from release of any hydrogen chloride was determined potentiometrically. No change in pH was observed for temperatures up to 180° C. In view of the great solubility of hydrogen chloride in water a complete absorption of any hydrogen chloride formed could be expected. Each ampoule with its contents was thoroughly crushed and brought into intimate contact with the water. With the quantity of DDT and water used, a decomposition to the extent of 0.5% would produce enough hydrogen chloride to lower pH to about 4.0. Even in the unlikely case of a very incomplete hydrogen chloride absorption of, for example, only 10%, the pH would still be lowered to about 5.0. A sample heated to 190° C. showed a large increase in acidity that, on the assumption that the only change brought about was dehydrochlorination of the *p–p'*-DDT molecule, indicated a decomposition of 7 to 8%. Another sample of pure *p–p'*-DDT, heated to 180° C. as above and then cooled and broken open in air, showed no change in melting point.

As DDT can be transferred by the sublimation process even when in the solid form (at 90–100° C. rather slowly), there is a considerable range of temperature that can be used for the application of DDT by this technique. The rate of transfer is, however, a function of the partial vapor pressure of the DDT and is increased at higher temperatures.

In the apparatus described a temperature of 160° C. was found convenient.

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